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Spatiotemporal variability of nitrous oxide in a large eutrophic estuarine system: The Pearl River Estuary, China

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ABSTRACT

The spatiotemporal variations of nitrous oxide (N_2O) in the Pearl River Estuary, a large perturbed estuary, were investigated via six cruises covering both wet and dry seasons during 2007–2011. Significant spatial and temporal variabilities in N_2O concentrations and N_2O saturations were detected. Spatially, N_2O was oversaturated in the entire estuary; ranging from 328 nmol L^{-1}, or 38 times saturation in the O_2-depleted Upper Estuary, down to 11–79 nmol L^{-1} in the Middle Estuary (163–905% saturation), and to ~7 nmol L^{-1} (slight supersaturation) in the Lower Estuary. Temporally, increased N_2O up to 182 ± 82 nmol L^{-1} (1800 ± 750% saturation) was observed in the Upper Estuary during winter at low river discharge in comparison to 76 ± 19 nmol L^{-1} (1163 ± 287% saturation) in summer at high river discharge; whereas no significant seasonal difference was detected within the Middle and Lower Estuaries. The N_2O fluxes decreased by 2 orders of magnitude from upstream to downstream (733 to lower than 5 μmol m^{-2} d^{-1}). Seasonally, the higher N_2O fluxes integrated across the estuary were in spring and winter, and lower fluxes were exhibited in summer and autumn. The annual water–air N_2O flux was estimated to be 37 ± 15 μmol m^{-2} d^{-1}. This rendered a total emission of (1.67 ± 0.89) × 10^9 g N_2O yr^{-1}, which is equivalent to the revised total emission from 19 European inner estuaries (1.35 × 10^9 g N_2O yr^{-1}). Moreover, this amount of N_2O emission equals approximately 30% of reported CO_2 emission from the Pearl River Estuary in terms of greenhouse warming potential. The N_2O production was predominantly modulated by nitrification in the Upper Estuary while in the Middle and Lower Estuaries, estuarine mixing appeared to dominate the N_2O behavior.

1. Introduction

Nitrous oxide (N_2O), a trace gas with a 114 year lifespan in the atmosphere, has about 300 times greater greenhouse potential relative to CO_2. It is increasing in concentration at a rate of ~0.25% annually due to increasing human activities (IPCC, 2007). Additionally, N_2O contributes to the destruction of stratospheric ozone (Ravishankara et al., 2009), and thus is an important gas component of the earth's climatic system (Bange, 2000).

N_2O is generated as a by-product from the first step of microbial nitrification, i.e. the oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) (Dore and Karl, 1996; Yoshinari et al., 1997; Middelburg and Nieuwenhuize., 2000). N_2O is also known to be produced as an intermediate from denitrification, i.e., the reduction of nitrate (NO_3^-) to N_2 (Naqvi et al., 2000; Walter et al., 2006; Yamagishi et al., 2007). Nitrification is principally autotrophic, whereas denitrification is heterotrophic. Both processes can occur either in the water column or sediments (Codispoti et al., 2001; Bange, 2008). In each case, the N_2O yield is believed to be highly dependent on the ambient dissolved O_2 concentration in aquatic systems (Goreau et al., 1980; Codispoti et al., 2001; Naqvi et al., 2010). N_2O production would be significantly enhanced under low O_2 concentrations (Dai et al., 2008; Codispoti, 2010; Naqvi et al., 2010; Kim et al., 2013).

Marine waters are generally believed to be a major natural and anthropogenic source of atmospheric N_2O (Seitzinger et al., 2000). Coastal aquatic systems, including estuaries, are an important component of the marine N_2O cycle. However, N_2O emissions from estuaries demonstrate considerable uncertainty (Bange et al., 1996; Bange, 2006; Nevison et al., 2003; Barnes and Upstill-Goddard, 2011) due to major spatiotemporal variability and the limited data available. In addition, most early estimates of estuarine N_2O emissions focused on relative small European estuaries (Bange et al., 1996; Bange, 2006; Barnes and Upstill-Goddard, 2011). Mounting evidence suggests that substantial differences occur in different estuarine systems, and the large Asian estuaries might hold an increasingly important role in budgeting the future global N_2O emission with increasing anthropogenic stress (Zhang et al., 2010; Rao and Sarma, 2013). Even within a single estuary, large spatiotemporal variations are present (Harley et al., 2015). This poses a big challenge to reliably constrain the estuarine N_2O effluxes at a global scale.

The Pearl River (Zhujiang) Estuary is a large subtropical Asian estuary altered significantly by human-induced perturbation (Dai et al.,

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2006, 2008, 2014; He et al., 2014). This estuary is located in one of the most rapidly developing areas of the world during the past three decades. The estuarine environment was greatly affected by the rapid economic growth and anthropogenic stress from cities such as Guangzhou, Hong Kong, Macau, Shenzhen, and Zhuhai. Many environmental issues, such as ammonium contamination and hypoxia, have emerged (Zhai et al., 2005; Dai et al., 2006, 2008; Guo et al., 2009; He et al., 2014). This coupled high-nitrogen and low-oxygen system permits an opportunity to examine nitrogen transformation and the production of N_2O.

We conducted six cruises during 2007–2011 to constrain the water–air N_2O fluxes from the Pearl River Estuary that encompasses both spatial and temporal variations. An estimate of N_2O effluxes into the atmosphere was conducted based on the seasonal and zonal distributions of N_2O distribution. These fluxes and emissions were compared with other estuaries in Asia and Europe. Factors regulating N_2O production were discussed as well.

2. Material and methods

2.1. Study area

The Pearl River is the second largest river in China in terms of annual water discharge (3.26×10^{11} m^3 yr^{-1}). It spans for 2214 km, and drains an area of 452,000 km^2 (Dai et al., 2014). The Pearl River has three main tributaries (Fig. 1); namely, the Xijiang (West River), Beijiang (North River), and Dongjiang (East River). Amongst them, the West River accounts for ~70% of the total freshwater discharge (China Bureau of Hydrology, Ministry of Water Resources, http://sqqx.hydroinfo.gov.cn/websq/). The water discharge rate shows significant seasonality, and ~80% of the discharge takes place in the wet season from April to September (Fig. 2). During winter, the monthly average river discharge is around 2000 m^3 s^{-1}. In contrast, the monthly average water flow rate during the summer can be 8 times higher; peaking at approximately 16,000 m^3 s^{-1} in June.

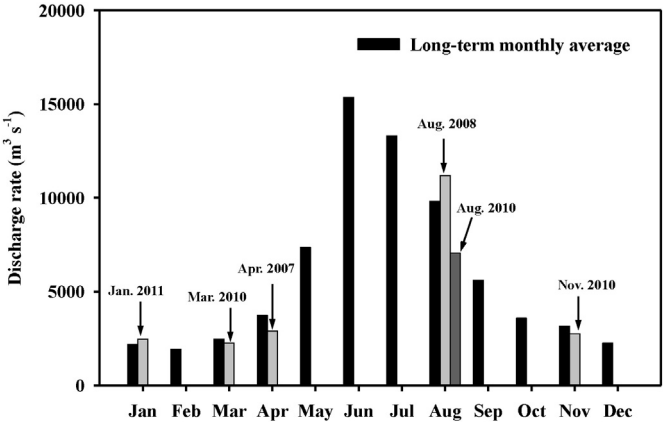

Fig. 2. Long-term monthly averaged water discharge from 2000 to 2011 at the Wuzhou hydrological station on the West River (China Bureau of Hydrology, Ministry of Water Resources, http://sqqx.hydroinfo.gov.cn/websq/). The monthly averaged discharge of survey cruises in April 2007, August 2008, March 2010, August 2010, November 2010, and January 2011 is also shown.

For the convenience of N_2O flux estimation, we divided the survey region (with a total area of ~2789 km^2) into 3 zones in accordance to the N_2O level and the geometry of the estuary similar to Guo et al. (2009) (Fig. 1). These 3 zones are (1) Upper Estuary: Guangzhou section, the channel flowing through the city of Guangzhou to Humen Outlet, with a length of ~75 km and an area of ~107 km^2; (2) Middle Estuary: Inner Lingdingyang, from Humen Outlet to Inner Lingding Island, with a length of ~40 km and an area of ~582 km^2; (3) Lower Estuary: Outer Lingdingyang, from Inner Lingding Island to the Outer Estuary, with a length of ~50 km and an area of ~2100 km^2 (Fig. 1, Table 1).

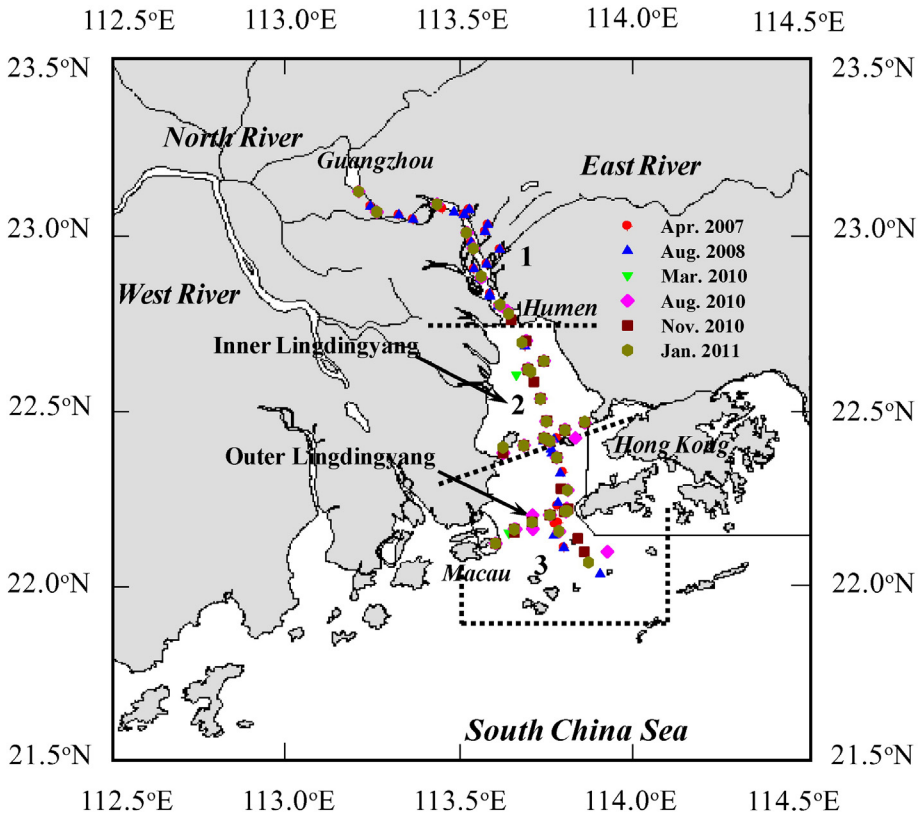

Fig. 1. Map of the Pearl River Estuary showing the sampling sites during 2007–2011. This study partitioned the estuary into 3 zones: (1) Upper Estuary (Humen upstream); (2) Middle Estuary (Inner Lingdingyang); (3) Lower Estuary (Outer Lingdingyang and beyond).